Adsorption (2008) 14: 85–92
DOI 10.1007/s10450-007-9057-x

Adsorption of Cr(VI) using activated neem leaves: kinetic studies

B.V. Babu · S. Gupta

Received: 13 December 2006 / Revised: 16 July 2007 / Accepted: 17 September 2007 / Published online: 4 October 2007

Abstract In the present study, adsorbent is prepared from neem leaves and used for Cr(VI) removal from aqueous solutions. Neem leaves are activated by giving heat treatment and with the use of concentrated hydrochloric acid (36.5 wt%). The activated neem leaves are further treated with 100 mmol of copper solution. Batch adsorption studies demonstrate that the adsorbent prepared from neem leaves has a significant capacity for adsorption of Cr(VI) from aqueous solution. The parameters investigated in this study include pH, contact time, initial Cr(VI) concentration and adsorbent dosage. The adsorption of Cr(VI) is found to be maximum (99%) at low values of pH in the range of 1-3. A small amount of the neem leaves adsorbent (10 g/l) could remove as much as 99% of Cr(VI) from a solution of initial concentration 50 mg/l. The adsorption process of Cr(VI) is tested with Langmuir isotherm model. Application of the Langmuir isotherm to the system yielded maximum adsorption capacity of 62.97 mg/g. The dimensionless equilibrium parameter, R_L, signifies a favorable adsorption of Cr(VI) on neem leaves adsorbent and is found to be between 0.0155 and 0.888 ($0 < R_L < 1$). The adsorption process follows second order kinetics and the corresponding rate constant is found to be 0.00137 g/(mg) (min).

Keywords Adsorption · Batch studies · Neem leaves · Kinetics · Isotherms

Abbreviations

b	Langmuir constant (l/mg)
C_0	initial concentration of Cr(VI) (mg/ml)
C_e	concentration of chromium at equilibrium (mg/ml)
k_{ad}	rate constant of the pseudo first-order adsorption process (min^{-1})
k_2	second-order rate constant (g/mg min)
q	amount of Cr(VI) adsorbed by the adsorbent (mg/g)
q_e	amount of Cr(VI) adsorbed at equilibrium by the adsorbent (mg/g)
q_t	amount of Cr(VI) adsorbed at time, t, by the adsorbent (mg/g)
V	initial volume of chromium solution (ml)
W	weight of the adsorbent (g)

1 Introduction

Chromium exists in two stable oxidation states, Cr(III) and Cr(VI). The Cr(VI) state is of particular concern because this form is hazardous to health. Chromium is introduced into the natural bodies of water from industries like electroplating, leather tanning, cement industries, steel industries, and photography. Cr(VI) causes skin irritation resulting in ulcer formation. Over exposure to Cr(VI) leads to liver damage, pulmonary congestion and oedema (Raji and Anirudhan 1998). The current maximum contamination level (MCL) for total chromium in drinking water in the U.S.A. is stipulated by the Environmental Protection Agency (EPA) to be 100 µg/l (Lalvani et al. 1998). So the elimination of Cr(VI) from drinking water is of great concern.

Various technologies are employed for removing toxic ions from water, which include chemical precipitation, reverse osmosis, ion-flotation, evaporation, ion-exchange and adsorption (Rawat and Singh 1992). Among these, adsorption is the most promising technique (Gupta and Babu

---

B.V. Babu (✉) · S. Gupta
Chemical Engineering Group, Birla Institute of Technology and Science (BITS), Pilani 333 031, Rajasthan, India
e-mail: bvbabu@bits-pilani.ac.in

2006). Studies on the sorption of Cr(VI) by activated carbon and various low cost materials have been reported (Bailey et al. 1999). Because of their large surface area and high porosity, activated carbons have been considered as potential adsorbents for Cr(VI) (Jianlong et al. 2000). The use of commercial activated carbon is not suitable because of its high cost. Therefore, there is a need to produce low cost adsorbent for Cr(VI) removal from cheaper and readily available materials which can be used economically on large scale. Recently, the removal of Cr(VI) from aqueous solution is studied by natural, low-cost materials such as sphagnum mass peat, saw dust, leaf mould, sugar beet pulp, bagasse, maize cob, biogas residual slurry, Fe(III)/Cr(III) hydroxide (Hu et al. 2003).

In the present study, adsorbent is prepared from neem leaves and studies are carried out for Cr(VI) removal. Neem leaves are activated by heat treatment and with the use of concentrated hydrochloric acid (36.5 wt%). The activated neem leaves are further treated with 100 mmol copper solution. Batch experiments are carried out for kinetic studies on the removal of Cr(VI) from aqueous solution. The effect of various parameters such as pH, contact time, initial concentration and adsorbent amount has been studied.

2 Experimental studies

2.1 Adsorbent preparation

Neem leaves are collected from institute campus (BITS-Pilani) neem trees. Neem leaves are washed repeatedly with distilled water to remove dust and soluble impurities. Initially leaves are kept for drying at room temperature in a shade for 6 h and then in an oven at 80 °C till they turn pale yellow. Then they are crushed and passed through 15-20 mesh BSS screens. Neem leaves are activated by treating one part of neem leaves with 1.8 parts by weight of concentrated HCl (36.5 wt%) and keeping it an oven at 150 °C for 24 h. The treated leaves are washed with distilled water to remove free acid and dried at 100 °C for 5 h. Then 10 g of activated neem leaves are treated with 100 ml of 100 mmol/L copper solution (initial pH 8.5). The mixture was shaken for 24 h at 30 °C and filtered with membrane filter paper. Copper impregnated neem leaves are washed several times with distilled water until the filtrate is free from copper. Finally, the adsorbent is dried at 80 °C for 6 h.

2.2 Batch experiments

All the chemicals used are of analytical grade. A stock solution of Cr(VI) is prepared by dissolving 2.8287 g of 99.9% potassium dichromate ($K_2Cr_2O_7$) in 1000 ml of distilled water. This solution is diluted as required to obtain standard solutions containing 20-700 mg/l of Cr(VI). 0.5 N HCl and 0.5 N NaOH solutions are used for pH adjustments.

The batch experiments are carried out in 100 ml borosil conical flasks by agitating a pre-weighed amount of the neem leaves adsorbent with 25 ml of the aqueous Cr(VI) solutions for a predetermined period at 30 °C on a water bath-cum-mechanical shaker. The adsorbent is separated with filter paper. Adsorption isotherm study is carried out with different initial concentrations of Cr(VI) from 40 to 700 mg/l while maintaining the adsorbent dosage at 10 g/l. The effect of time and pH are studied at 30 °C with a Cr(VI) concentration of 50 mg/l and an adsorbent dosage of 10 g/l. The effect of adsorbent amount is studied by varying the adsorbent amount from 4 g/l to 16 g/l with a Cr(VI) concentration of 50 mg/l.

The concentration of free Cr(VI) ions in the effluent is determined spectrophotometrically by developing a purple-violet color with 1,5-diphenyl carbazide in acidic solution as an complexing agent (APHA 1985). The absorbance of the purple-violet colored solution is read at 540 nm after 20 min.

The amount of chromium adsorbed by the activated neem leaves is calculated using the following equation:

$$q = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where, q amount of Cr(VI) adsorbed by the adsorbent (mg/g), C_0 initial concentration of Cr(VI) (mg/ml), C_e concentration of chromium at equilibrium (mg/ml), V initial volume of chromium solution (ml), W weight of the adsorbent (g).

3 Results and discussion

In the present study, it is found that, using the neem leaf powder as an adsorbent, for the 50 mg/l of initial concentration of Cr(VI) and 10 g/l of adsorbent dosage, the percentage removal of Cr(VI) obtained to be 99% as compared to 88% reported by Sharma and Bhattacharyya (2004). Table 1 shows the comparison of adsorbent capacity of various adsorbents. When compared with other costly and low cost adsorbents, the results of the present study indicate that adsorbent prepared from neem leaves has better adsorption capacity in almost all cases (S. Nos. 4-23 in Table 1) except for activated carbon (GA-3) and activated carbon (SHT) (S. Nos. 1-2 in Table 1). In an adsorption process, atoms, ions or molecules of an adsorbate diffuse to surface of a solid, where they either bond with the solid surface or are held thereby weak intermolecular forces. The electrostatic, chemisorptive and functional group interactions define the affinity of an adsorbent for a specific adsorbate. In the present study, activated neem leaves is used as an adsorbent for the removal of Cr(VI) from aqueous solution. The adsorption kinetic study for the removal of metal ions from

Table 1 Summary of adsorbent capacity of various adsorbents

S No	Adsorbent	Maximum adsorbent capacity, q_m(mg/g)	Optimum pH	Reference
1	Activated carbon (GA-3)	69.3	3.2	Hu et al. (2003)
2	Activated carbon (SHT)	69.1	3.2	Hu et al. (2003)
3	Neem leaves	62.97	2	Present study
4	Activated carbon (Filtrasorb-400)	57.7	–	Huang and Wu (1977)
5	Sawdust	39.7	2.0	Sharma and Forster (1994)
6	Tamarind seeds	29.7	2.0	Gupta and Babu (2006)
7	Coconut husk fiber	29	2.05	Tan et al. (1993)
8	Leaf mould	25.9	2.5	Sharma and Forster (1996)
9	Pine needles	21.50	2.0	Dakiky et al. (2002)
10	Coconut shell based activated carbon	20	2.5	Alaerts et al. (1989)
11	Sugar beet pulp	17.2	2.0	Sharma and Forster (1994)
12	Palm pressed-fibers	15.0	2.0	Tan et al. (1993)
13	Maize cob	13.8	1.5	Sharma and Forster (1994)
14	Sugar cane bagasse	13.4	2.0	Sharma and Forster (1994)
15	Almond	10	2.0	Dakiky et al. (2002)
16	Maple saw dust	8.2	4.0	Li et al. (2003)
17	Cactus	7.08	2.0	Dakiky et al. (2002)
18	Coal	6.78	2.0	Dakiky et al. (2002)
19	Biomass residual slurry	5.87	2.0	Namasivayam and Ranganathan (1993)
20	Distillery sludge	5.7	2.5	Selvaraj et al. (2003)
21	Waste tea	1.55	–	Orhan and Buyukgungur (1993)
22	Fe(III)/Cr(III) hydroxide	1.43	5.7	Namasivayam and Ranganathan (1993)
23	Walnut shell	1.33	–	Orhan and Buyukgungur (1993)
24	Soya cake	0.28	1	Daneshvar et al. (2002)

wastewater is important in getting the insight into the adsorption mechanism. The adsorption process mechanism for the solute transport onto the adsorbent surface follows three steps: (i) external mass transfer of solute from the bulk fluid to the film surrounding the adsorbent (ii) from film to the adsorbent surface and (iii) from surface to the internal sites followed by binding of metal ions to the active sites. Generally it is observed that, the rate of adsorption process is controlled by either step (ii) or step (iii). It is reported in the literature that the physical attachment of adsorbate to adsorbent is not the actual rate controlling step (Sharma and Bhattacharyya 2004). In fact, the adsorption of adsorbate on adsorbent also depends on the surface available. In the present study, specific surface area of activated neem leaves is measured as 15.284 m^2/g by High Speed Gas Sorption Analyzer (Quantachrome Corporation NOVA 1000, Version 6.07). Specific surface area of activated neem leaves is 10 times more than the specific surface area (1.3 m^2/g) of neem leaf powder reported by Sharma and Bhattacharyya (2004). This increase in specific surface area is one of the important reason for the higher uptake of Cr(VI) on activated neem leaves. Cr(VI) adsorption also depends on both microporous structure and surface functionality (Park and Jang 2002). The adsorption of Cr(VI) is more effective on acid-treated adsorbents (Mattson and Mark 1971). Neem leaves are activated using concentrated hydrochloric acid at 150 °C. At this temperature, activated neem leaves generally develop acidic surface oxides and lower solution pH. At lower pH, dominant form of Cr(VI) is $HCrO_4^-$ while the surface of adsorbent is charged positively. The following reaction mechanism for adsorption of Cr(VI) at different pH is proposed by Bayat (2002).

$$\begin{aligned} 2H^+ + 2HCrO_4^- &\xleftrightarrow{2H^+} 2H_2CrO_4 \longleftrightarrow 2H_2O + Cr_2O_7^{2-} \\ &\xleftrightarrow{2H^+} 2CrO_3 + H_2O \end{aligned} \tag{2}$$

The H_2CrO_4 and CrO_3 exist as polynuclear species at high chromium concentration and at low pH value. Based on the above results obtained, the effect of various parameters such as pH, contact time, initial concentration, and adsorbent dosage has been studied.

3.1 Effect of pH

The pH of the aqueous solution is a significant parameter for the removal of metal ions by adsorption (Sanches-Polo

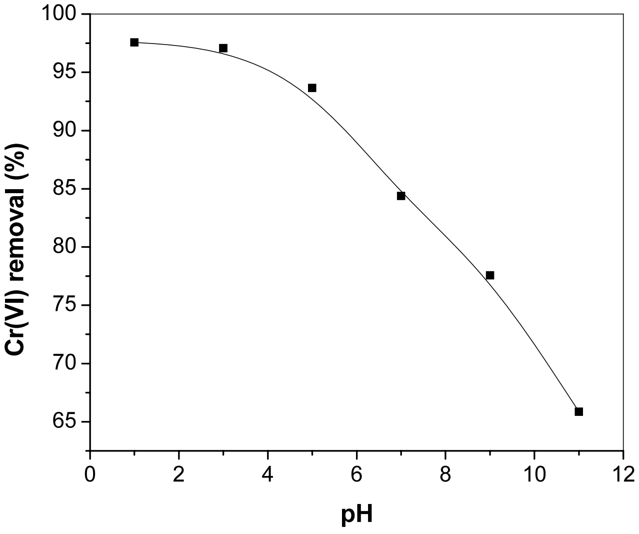

Fig. 1 Effect of pH on Cr(VI) adsorption

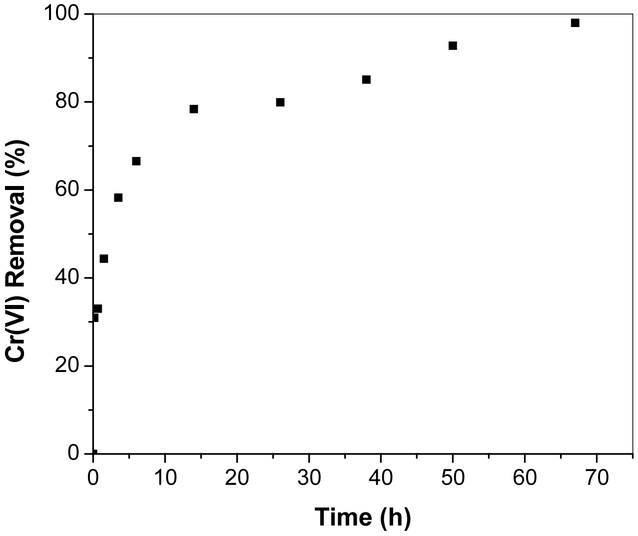

Fig. 2 Effect of contact time on Cr(VI) adsorption

and Rivera-Utrilla 2002). In the present work, adsorption of Cr(VI) is studied in the initial pH range of 1-11. The effect of initial pH on Cr(VI) removal is shown in Fig. 1. Removal efficiency increased from 65.8% (initial pH = 11) with decreasing initial pH and reached 98% in the initial pH range of 1-3. Cr(VI) may exist in the aqueous phase in different anionic forms such as chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), or hydrogen chromate ($HCrO_4^-$) as given by (2). It is well known that the dominant form of Cr(VI) at lower pH is $HCrO_4^-$ (Namasivayam and Ranganathan 1993). Increasing the pH will shift the concentration of $HCrO_4^-$ to other forms (CrO_4^{2-} and $Cr_2O_7^{2-}$). It can be concluded that the active form of Cr(VI) that can be adsorbed by the adsorbent in this study is $HCrO_4^-$.

3.2 Effect of contact time

Figure 2 shows the effect of contact time for the adsorption of Cr(VI) on neem leaves. It is evident that time has a significant influence on the adsorption of Cr(VI). It is apparent from Fig. 2 that till 12 h, the percentage removal of Cr(VI) from aqueous solution increases rapidly and reaches up to 77%. After that, the percentage removal of Cr(VI) increases slowly till 67 h and reaches up to 98%. A further increase in contact time has a negligible effect on the percentage removal. Therefore, the contact time of 67 h could be considered for adsorption of Cr(VI) on neem leaves for entire batch studies. The mechanism of solute transfer to the solid includes diffusion through the fluid film around the adsorbent particle and diffusion through the pores to the internal adsorption sites. Initially the concentration gradient between the film and the solid surface is large, and hence the transfer of solute onto the solid surface is faster. That is why it takes lesser time to attain percentage removal of Cr(VI) up to 77%. As time increases, intraparticle diffusion becomes predominant. Hence solute takes more time to transfer from solid surface to internal adsorption sites through the pores.

3.3 Effect of initial concentration

Cr(VI) adsorption is significantly influenced by the initial concentration of Cr(VI) in aqueous solutions. In the present study, the initial Cr(VI) concentration is varied from 40 to 700 mg/l while maintaining the adsorbent dosage at 10 g/l. Figure 3 shows the effect of initial concentration on percentage removal of Cr(VI) and adsorption capacity of activated neem leaves. The percentage removal decreases from 99.95% to 89.94% and adsorption capacity increases from 3.98 to 62.9 mg/g when Cr(VI) concentration increases from 40 to 700 mg/l with the same contact time and adsorption temperature. The percentage removal of Cr(VI) decreases with an increase in initial Cr(VI) concentration. It may be due to an increase in the number of Cr(VI) ions for the fixed amount of adsorbent. The amount of Cr(VI) adsorbed per unit mass of activated neem leaves increases with increase in Cr(VI) concentration, may be due to the complete utilization of adsorption surface and active sites available which is not possible in low concentration. For the initial Cr(VI) concentration value of 505 mg/l, the optimum values of Cr(VI) removal and adsorption capacity are found to be 97.6% and 49.2 mg/g, respectively.

3.4 Effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption of Cr(VI) process is shown in Fig. 4. Removal of Cr(VI) increases with an increase in the adsorbent dosage. The percentage removal increases from 99.5 to 99.9% by increasing the adsorbent dosage from 4 to 16 g/L. However, the adsorption

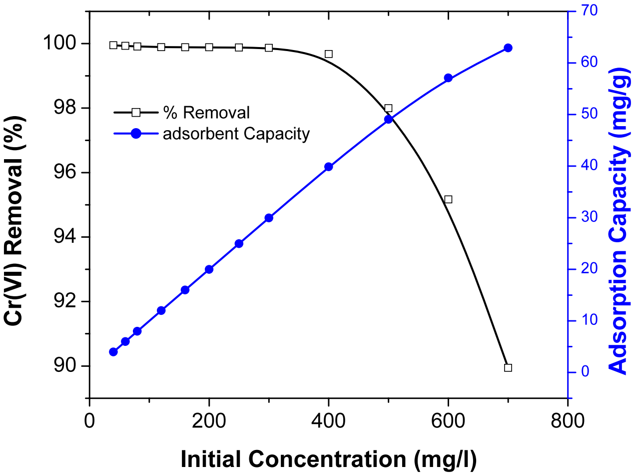

Fig. 3 Effect of initial concentration on Cr(VI) adsorption

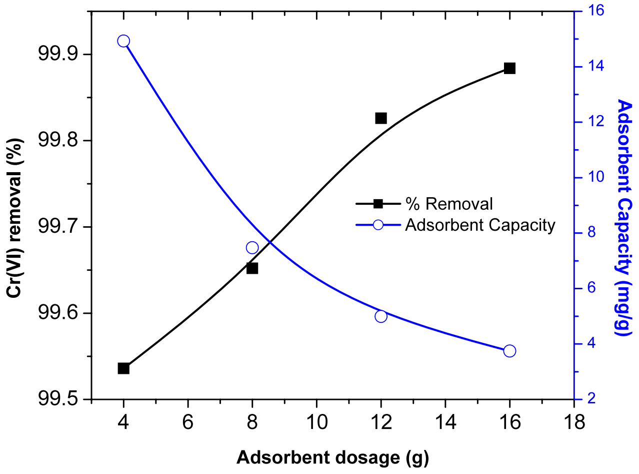

Fig. 4 Effect of adsorbent dosage on Cr(VI) adsorption

capacity showed a decreasing trend with increasing adsorbent dosage. If the adsorbent amount is increased by keeping the Cr(VI) concentration constant, the amount of Cr(VI) adsorbed per unit mass showed a decrease due to availability of less number of Cr(VI) ions per unit mass of the adsorbent. The adsorption capacity dropped from 14.9 to 3.74 mg/g by increasing the adsorbent dosage from 4 to 16 g/L. The drop in adsorption capacity is basically due to the sites remaining unsaturated during the adsorption process. For the 8.5 g/l of adsorbent dosage, the optimum values of Cr(VI) removal and adsorption capacity are found to be 99.6% and 7.6 mg/g, respectively.

3.5 Adsorption isotherms

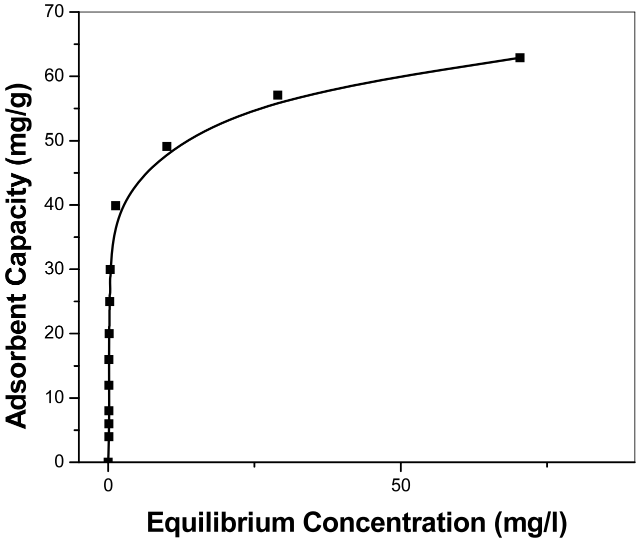

Fig. 5 Adsorption isotherm for Cr(VI) adsorption on neem leaves

If a quantity, q, of adsorbate is adsorbed by a porous solid at constant temperature and the steady state equilibrium concentration, c, then the function $q(c)$ describes the adsorption isotherm. Figure 5 shows the adsorption isotherm for the Cr(VI) adsorption on neem leaves. A variety of isotherm equations have been in use, some of which have a theoretical foundation and some being of mere empirical nature. In the present work, Langmuir isotherm has been tested.

3.5.1 Langmuir isotherm

This isotherm is applicable when the extent of adsorbate coverage is limited to one molecular layer. The isotherm assumes a dynamic equilibrium between the adsorbed phase and the liquid phase. Langmuir described chemisorption as the formation of an ionic or covalent bond between adsorbent and adsorbate. The isotherm equation gives the fractional coverage (θ) in the form

$$\theta = \frac{q_\mathrm{e}}{q_\mathrm{m}} = \frac{bC_\mathrm{e}}{1+bC_\mathrm{e}} \tag{3}$$

where, the parameter $b = k_\mathrm{a}/k_\mathrm{d}$, where k_a and k_d are the respective constants for adsorption and desorption, respectively and q_m is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent and q_e is the amount adsorbed on unit mass of the adsorbent when the equilibrium concentration is C_e. Equation (3) can be rearranged to the form:

$$\frac{C_\mathrm{e}}{q_\mathrm{e}} = \frac{1}{bq_\mathrm{m}} + \left(\frac{1}{q_\mathrm{m}}\right)C_\mathrm{e} \tag{4}$$

This shows that a plot of $(C_\mathrm{e}/q_\mathrm{e})$ vs. C_e should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium. The slope and the intercept of this line then give the values of q_m and b.

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L

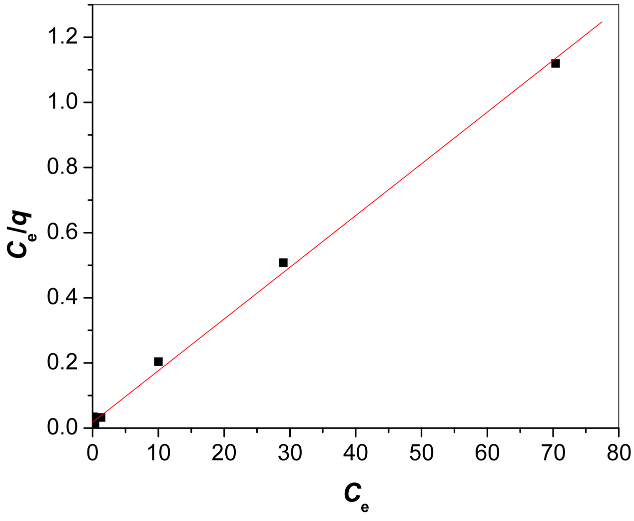

Fig. 6 Langmuir isotherm for adsorption of Cr(VI)

(Hall et al. 1966), also known as the separation factor, given by

$$R_L = \frac{1}{1 + bC_e} \tag{5}$$

The value of R_L lies between 0 and 1 for favorable adsorption, while $R_L > 1$ represents unfavorable adsorption, and $R_L = 1$ represents linear adsorption while the adsorption process is irreversible if $R_L = 0$.

The isotherm data has linearized using the Langmuir equation and shown in Fig. 6. The high value of correlation coefficient ($R^2 = 0.998$) indicated a good agreement between the parameters and confirms the monolayer adsorption of Cr(VI) onto the adsorbent surface. The constant q_m, which is a measure of the adsorption capacity to form a monolayer, can be as high as 62.97 mg/g in the initial pH range of 1-3. The constant b, which denotes adsorption energy, is equal to 0.904 l/mg. The dimensionless parameter, R_L, remained between 0.0155 and 0.888 ($0 < R_L < 1$) consistent with the requirement for a favorable adsorption process.

3.6 Adsorption kinetics

Several kinetic models are in use to explain the mechanism of the adsorption processes. A simple pseudo first-order equation due to Lagergren was used by Ho and Mckay (1998, 1999):

$$\frac{dq_t}{dt} = k_{ad}(q_e - q_t) \tag{6}$$

Where q_e and q_t are the amount of adsorption at equilibrium and at time t respectively, and k_{ad} is the rate constant of the pseudo first-order adsorption process. The integrated rate law after application of the initial condition of $q_t = 0$ at $t = 0$, becomes:

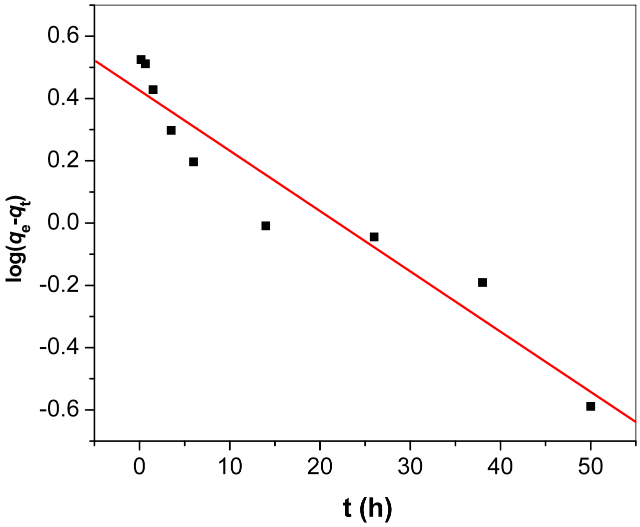

Fig. 7 Lagergren plot for the adsorption of Cr(VI) by neem leaves for adsorbent dosage, 10 g/l; concentration 50 mg/l; initial pH, 2.0; and temperature, 30 °C

$$\log(q_e - q_t) = \log q_e - k_{ad}t/2.303 \tag{7}$$

Plot of $\log(q_e - q_t)$ vs. t gives a straight line for first order adsorption kinetics, which allow computation of the adsorption rate constant, k_{ad}. Linear plot between $\log(q_e - q_t)$ and t is shown in Fig. 7. The k_{ad} and q_e value for the initial concentration of 50 mg/l are found to be 7.434×10^{-4} min^{-1} and 2.66 mg/g. The true value of q_e obtained from experiments is 4.86 mg/g. Comparison between obtained and true value of q_e shows that the pseudo first-order kinetics is inadequate to give a good account of the kinetics of Cr(VI) adsorption on neem leaves.

This equation (6) differs from a true first order equation in two ways: (i) the parameter $k_{ad}(q_e - q_t)$ does not represent the number of available sites, and (ii) the parameter $\log(q_e)$ is an adjustable parameter and often it is found to be not equal to the intercept of the plot of $\log(q_e - q_t)$ vs. t, whereas in a true first order $\log q_e$ should be equal to the intercept. In such cases, applicability of the second order kinetics has to be tested with the rate equation (Sharma and Bhattacharyya 2004; Ozturk and Kavak 2005):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{8}$$

where k_2 is the second order rate constant in g/(mg)(min). From the boundary conditions, $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of the equation becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{9}$$

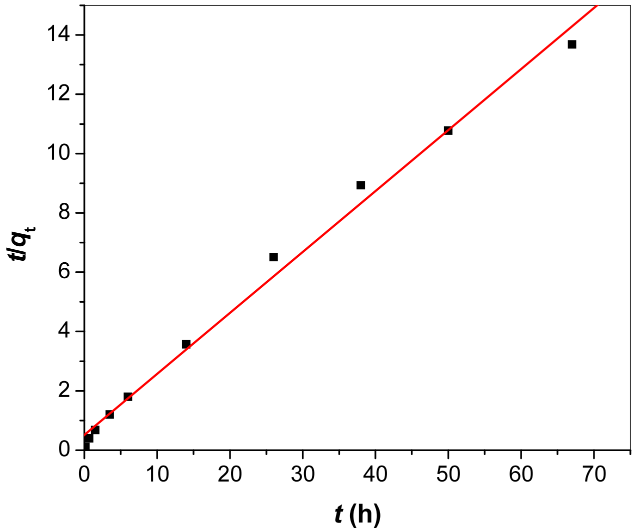

Fig. 8 Second-order plot for the adsorption of Cr(VI) by neem leaves seeds for adsorbent dosage, 10 g/l; concentration 50 mg/l; initial pH, 2.0; and temperature, 30 °C

which can be written in the linear form,

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right)t \qquad (10)$$

where $h = k_2 q_e^2$ can be regarded as the initial sorption rate as $t \to 0$. Under such circumstances, the plot of t/q_t vs. t should give a linear relationship, which allows computation of q_e, k and h.

Application of second order kinetics by plotting t/q_t vs. t, (10) yielded better results shown in Fig. 8. There is also now good agreement between experimental ($q_e = 4.86$) values and those obtained from the slope ($q_e = 4.87$) of the second order plots. The second-order rate constant is found to be 0.00137 g/(mg) (min).

4 Conclusion

Use of adsorbent prepared from neem leaves is capable and cost effective for the removal of Cr(VI) from aqueous solution. It is found that after activation with concentrated hydrochloric acid, increase in specific surface area and development of acid base surface have significant influence on the Cr(VI) adsorption. The maximum adsorption of chromium (VI) took place in the initial pH range of 1-3. The active form of Cr(VI) that can be adsorbed onto the activated neem leaves at lower pH is found to be $HCrO_4^-$. The percentage removal of Cr(VI) decreases as the pH increases. The kinetic studies indicated that the Cr(VI) adsorption on to the activated neem leaves is very fast (within first 12 h), while equilibrium is reached in 67 h. Percentage removal increases and adsorption capacity decreases with increase in adsorbent amount because of availability of more unsaturated adsorption sites. The equilibrium adsorption data are satisfactorily fitted with Langmuir isotherm model which confirms the monolayer adsorption of Cr(VI) onto the activated neem leaves surface. The maximum adsorption capacity obtained from Langmuir isotherm model is 62.97 mg/g, which is higher than the other low cost adsorbents. The calculated value of the dimensionless separation factor from the Langmuir constant confirm favorable adsorption of Cr(VI) onto activated neem leaves. Adsorption of Cr(VI) follows the second order rate equation.

References

Alaerts, G.J., Jitjaturant, V., Kelderman, P.: Use of coconut shell based activated carbon for chromium (VI) removal. Water Sci. Technol. **21**, 1701–1704 (1989)

APHA: Standard Methods for the Examination of Water and Wastewater, 16th edn. APHA, AWWA, WPCF, Washington (1985)

Bailey, S.E., Olin, T.J., Bricka, R.M., Adrian, D.D.: A review of potentially low-cost sorbents for heavy metals. Water Res. **33**, 2469–2479 (1999)

Bayat, B.: Comparative study of adsorption properties of Turkish fly ashes. II. The case of chromium(VI) and cadmium(II). J. Hazard. Mater. **95**, 275–290 (2002)

Dakiky, M., Khamis, M., Manassra, A., Mer'eb, M.: Selective adsorption of chromium(VI) in industrial wastewater using low-cost abundantly available adsorbents. Adv. Environ. Res. **6**, 533–540 (2002)

Daneshvar, N., Salari, D., Aber, S.: Chromium adsorption and Cr(VI) reduction to trivalent chromium in aqueous solutions by soya cake. J. Hazard. Mater. B **94**, 49–61 (2002)

Gupta, S., Babu, B.V.: Adsorption of chromium(VI) by a low-cost adsorbent prepared from tamarind seeds. In: Proceedings of International Symposium & 59th Annual Session of IIChE in association with International Partners (CHEMCON-2006), GNFC Complex, Bharuch, December 27–30, 2006

Hall, K.R., Eagleton, L.C., Acrivos, A., Vermeulen, T.: Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions. Ind. Eng. Chem. Fundam. **5**, 212–219 (1966)

Ho, Y.S., Mckay, G.: A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. Trans. IChemE **76B**, 332–340 (1998)

Ho, Y.S., Mckay, G.: Comparative sorption kinetic studies of dyes and aromatic compounds onto fly ash. J. Environ. Sci. Health **A34**, 1179–1204 (1999)

Huang, C.P., Wu, M.H.: The removal of chromium (VI) from dilute aqueous solution by activated carbon. Water Res. **11**, 673–679 (1977)

Hu, Z., Lei, L., Li, Y., Ni, Y.: Chromium adsorption on high-performance activated carbons from aqueous solution. Sep. Purif. Technol. **31**, 13–18 (2003)

Jianlong, W., Xinmin, Z., Yi, Q.: Removal of Cr(VI) from aqueous solution by macroporous resin adsorption. J. Environ. Sci. Health **35**(7), 1211–1230 (2000)

Lalvani, S.B., Wiltowski, T., Hubner, A., Weston, A., Mandich, N.: Removal of hexavalent chromium and metal cations by a selective and novel carbon adsorbent. Carbon **36**, 1219–1226 (1998)

Li, J.Y., Shukla, S.S., Kenneth, L.D., Shukla, A., Margrave, J.L.: Adsorption of chromium from aqueous solutions by maple sawdust. J. Hazard. Mater. B **100**, 53–63 (2003)

Mattson, J.S.: Mark Jr., H.B.: Activated Carbon, Dekker, New York (1971)

Namasivayam, C., Ranganathan, K.: Waste Fe(III)/Cr(III) hydroxide as adsorbent for the removal of Cr(VI) from aqueous solution and chromium plating industry wastewater. Environ. Pollut. **82**, 255–261 (1993)

Orhan, Y., Buyukgungur, H.: The removal of heavy metals by using agricultural wastes. Water Sci. Technol. **28**, 247–255 (1993)

Ozturk, N., Kavak, D.: Adsorption of boron from aqueous solutions using fly ash: Batch and column studies. J. Hazard. Mater. B **127**, 81–88 (2005)

Park, S.J., Jang, Y.S.: Pore structure and surface properties of chemically modified activated carbons for adsorption mechanism and rate of Cr(VI). J. Colloid Interface Sci. **249**, 458–463 (2002)

Raji, C., Anirudhan, T.S.: Batch Cr(VI) removal by polyacrylamide-grafted sawdust: kinetics and thermodynamics. Water Res. **32**, 3772–3780 (1998)

Rawat, N.S., Singh, D.: Removal of chromium (VI) on bituminous coal. Asian Environ. **14**, 30–41 (1992)

Sanches-Polo, M., Rivera-Utrilla, J.: Adsorbent-adsorbate interactions in the adsorption of Cd(II) and Hg(II) on ozonized activated carbon. Environ. Sci. Technol. **36**, 3850–3854 (2002)

Selvaraj, K., Manonmani, S., Pattabhi, S.: Removal of hexavalent chromium using distillery sludge. Bioresour. Technol. **89**, 207–211 (2003)

Sharma, A., Bhattacharyya, K.G.: Adsorption of chromium (VI) on Azadirachta indica (neem) leaf powder. Adsorption **10**, 327–338 (2004)

Sharma, D.C., Forster, C.F.: A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents. Bioresour. Technol. **47**, 257–264 (1994)

Sharma, D.C., Forster, C.F.: A comparison of the sorbtive characteristics of leaf mould and activated carbon columns for the removal of hexavalent chromium. Process. Biochem. **31**, 213–218 (1996)

Tan, W.T., Ooi, S.T., Lee, C.K.: Removal of chromium (VI) from solution by coconut husk and palm pressed fibres. Environ. Technol. **14**, 277–282 (1993)